

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US05/004198

International filing date: 09 February 2005 (09.02.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/546,117
Filing date: 19 February 2004 (19.02.2004)

Date of receipt at the International Bureau: 31 March 2005 (31.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1297924

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

March 18, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: 60/546,117

FILING DATE: February 19, 2004

RELATED PCT APPLICATION NUMBER: PCT/US05/04198



Certified by

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office



Docket Number **3281B**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PROVISIONAL APPLICATION COVER SHEET

Wickliffe, Ohio
Dated: February 19, 2004



Mail Stop Provisional Patent Application
Hon. Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

(A) The attached document is filed as a PROVISIONAL APPLICATION for patent under 37 CFR 1.53 (b)(2).

(B) Inventors (*including* city and state or foreign country of residence, for each):

Joseph G. Seebauer, Willoughby, Ohio

Kathleen O. Havelka, Mentor, Ohio

(C) Title: Improving the Lipophilic Properties of 2-Acrylamido-2-Methylpropanesulfonic Acid

(D) Attorney: David M. Shold, Reg. no. 31,664

(E) Docket Number: 3281B

(F) Send Correspondence to: Docket Clerk

Patent Department
The Lubrizol Corporation
29400 Lakeland Blvd.
Wickliffe, Ohio 44092

(G) Fees: Charge the fee for filing of a provisional application, believed to be \$160.00, to deposit account 12-2275 (The Lubrizol Corporation). Any deficiency or overpayment in fees should be charged or credited to the same account.

Respectfully submitted,

David M. Shold
Attorney for Applicant
Reg. No. 31,664

Telephone: (440) 347-1601
Telefax: (440) 347-1110

I certify that this correspondence is being deposited with the United States Postal Service as express mail in an envelope addressed to: Hon. Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450, on:

February 19, 2004

Express Mail # ER169814166US

By: Shanda E. Kelly

Date: 2/19/04

PROVISIONAL PATENT APPLICATION

TITLE

IMPROVING THE LIPOPHILIC PROPERTIES OF
2-ACRYLAMIDO-2-METHYLPROPANESULFONIC ACID

FIELD OF THE INVENTION

[0001] The present invention relates to a method for improving the lipophilic properties of certain ethylenically unsaturated water-soluble monomers. Specifically, the invention relates to a method for improving the lipophilic properties of ethylenically unsaturated water-soluble sulfonic acid monomers. Further, this improvement will result in sulfonic acid monomers with enhanced compatibility with lipophilic, water-insoluble solvents and monomers. The enhanced compatibility will result in improved incorporation of the sulfonic acid monomer into emulsion polymers and lipophilic, solvent-based solution polymers. The improved sulfonic acid monomer incorporation will give benefits such as improved thermal stability, improved divalent cation resistance, improved pH stability, and improved mechanical stability to the emulsion polymers and lipophilic, solvent-based, water-insoluble, solution polymers containing it.

BACKGROUND OF THE INVENTION

[0002] Hydrophilic monomers such as certain ethylenically unsaturated water-soluble sulfonic acid monomers bring specific, beneficial properties such as, but not limited to, hydrophilicity, improved divalent cation stability, improved thermal stability, ionic strength, and polarity to polymers in which they are incorporated. These sulfonic acid monomers are well known; for example, 2-acrylamido-2-methylpropanesulfonic acid and its salts are well known materials which are commercially available under the trade name AMPS[®] monomers. Such materials and their methods of preparation are disclosed, for instance, in U.S. Patent 3,544,597. However, they are limited in their polymer applicability because of their poor lipophilic properties. They are not appreciably soluble in lipophilic solvents such as toluene or in lipophilic, water-insoluble monomers such as styrene or butyl acrylate. These poor lipophilic properties result in poor sulfonic acid monomer incorporation in polymers made in lipophilic solvents, thus limiting the beneficial properties derived from the sulfonic acid monomer.

[0003] In the process of incorporating ethylenically unsaturated water-soluble sulfonic acid monomers into polymer backbones of polymers made via emulsion polymerization, the poor lipophilic properties of the ethylenically

unsaturated water-soluble sulfonic acid monomer limit its incorporation into the emulsion polymer backbone typically composed of lipophilic, water-insoluble monomers such as styrene or butyl acrylate. This limits the beneficial properties, as described above, that the emulsion polymer could have.

5 [0004] It would be desirable if there were a method for improving the lipophilic properties of ethylenically unsaturated water-soluble sulfonic acid monomers. The improved sulfonic acid monomers would then have improved incorporation into lipophilic solution polymers and emulsion polymers leading to enhanced beneficial properties brought to the polymer by the sulfonic acid
10 monomer unit.

SUMMARY OF THE INVENTION

[0005] The present invention provides a method for improving the lipophilic properties of ethylenically unsaturated, water-soluble sulfonic acid monomers such as 2-acrylamido-2-methylpropanesulfonic acid, by forming salts of the
15 ethylenically unsaturated, water-soluble sulfonic acid monomers with lipophilic amines. The improved lipophilic properties will lead to improved incorporation of the sulfonic acid monomer unit into emulsion polymers and lipophilic, solvent based polymers. Said improved incorporation will give certain benefits to the emulsion polymers and lipophilic solvent based polymers. Benefits such
20 as improved thermal stability, improved divalent cation stability, improved mechanical stability, improved pH stability, and improved adhesion, have long been desired by those skilled in the art. However, these benefits have been difficult to achieve due to the poor lipophilic properties of the ethylenically unsaturated, water-soluble sulfonic acid monomers and their metallic salts. The
25 poor lipophilic properties limit the use of ethylenically unsaturated, water-soluble sulfonic acid monomers in solvent based polymers and their incorporation into emulsion polymers.

[0006] The present invention also provides a process for improving incorporation of ethylenically unsaturated water-soluble polymerizable sulfonic acid
30 into an emulsion polymer by adding the lipophilic amine salt of said ethylenically unsaturated water-soluble polymerizable sulfonic acid to a latex formulation. The process comprises the steps of (i) combining (a) a lipophilic monomer mixture consisting of one or more water-insoluble lipophilic monomers, (b) optionally an anionic surfactant, (c) 0.5 to about 40 weight percent, based on the
35 total monomers, of a lipophilic amine salt of an ethylenically unsaturated water-soluble polymerizable sulfonic acid, (d) water, (e) a polymerization initiator, (f) optionally an ethylenically unsaturated water-soluble polymerizable non-ionic

monomer, (g) optionally a chain transfer agent, and (h) optionally a buffer; and (i) heating the mixture to an appropriate temperature to effect the polymerization.

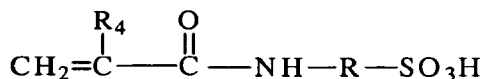
[0007] The present invention, therefore, solves the problem of incorporating a greater proportion of ethylenically unsaturated, water-soluble sulfonic acid monomers into lipophilic solvents for a variety of uses including polymerization with ethylenically unsaturated lipophilic water-insoluble monomers, as well as the problem of poor incorporation into emulsion polymers made with ethylenically unsaturated lipophilic water-insoluble monomers, by forming salts of the ethylenically unsaturated, water-soluble sulfonic acid monomers with lipophilic amines and using said salts in said various uses including polymerization.

DETAILED DESCRIPTION OF THE INVENTION

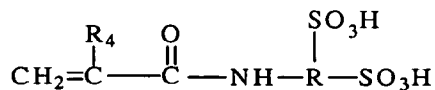
[0008] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0009] The method for improving the lipophilic properties of ethylenically unsaturated, water-soluble sulfonic acid monomers involves forming a salt of the sulfonic acid monomer with a lipophilic amine. This salt can then be used in a polymerization process, either an emulsion polymerization or a solvent based polymerization, both of which typically use water-insoluble monomers to polymerize with the sulfonic acid monomer. The terms polymer, polymerize, and polymerization, as used herein, are intended to broadly include polymer chains of two, three or more monomers, typically called copolymers, terpolymers, etc., and the reactions and processes to form these materials from mixtures of two, three or more ethylenically unsaturated monomers.

[0010] The ethylenically unsaturated, water-soluble sulfonic acid monomers usable in the present invention include polymerizable sulfonic acids such as acrylamido or methacrylamido sulfonic acids represented by the formulas:

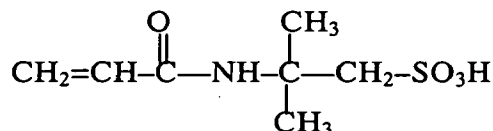


or



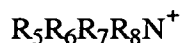
wherein R_4 is a hydrogen or a methyl group and R is an aliphatic or aromatic hydrocarbon group typically containing 2 to 8 carbon atoms. In one embodiment, the ethylenically unsaturated water-soluble polymerizable sulfonic acid

can be an unsaturated-hydrocarbylamido-alkanesulfonic acid. In the above structures, the R group can be branched, as in the molecule 2-acrylamido-2-methylpropanesulfonic acid, which has the following structure:



The R group can also include phenyl groups, alkyl substituted phenyl groups and cycloaliphatic groups.

[0011] The salts are selected from the group consisting of lipophilic amine salts. The amine ion can be represented by:



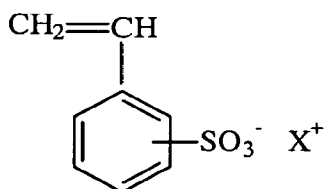
where R_5 , R_6 , R_7 , and R_8 are independently hydrogen or hydrocarbyl groups, provided that at least one of R_5 , R_6 , R_7 , and R_8 is a hydrocarbyl group of sufficient length suitable to impart lipophilic properties. The term "amine salt" or "amine ions" includes ions or salts, where up to three of the R groups are hydrocarbyl groups, and quaternary amine ions or salts, where each of the R groups is a hydrocarbyl group. In order to provide suitable lipophilic character, the total carbon atoms in the amine ion should be at least 6, preferably at least 10, and more preferably at least 14. It is preferred that the total number of carbon atoms in an amine cation does not exceed 36 carbon atoms. Examples of suitable amines include N,N-dimethyl-n-dodecylamine, 2-ethylhexylamine, tri-n-butylamine, triisobutylamine, triisooctylamine, tripropylamine, trihexylamine, trioctylamine, decylamine, dodecylamine, tridecylamine, tridodecylamine, hexadecylamine, octadecylamine, and oleylamine.

[0012] As used herein, the term "lipophilic" is given its conventional meaning, that is, interacting favorably with or being soluble in non-polar or fatty solvents. A synonym for "lipophilic" is "hydrophobic," which may be contrasted with "hydrophilic." Hydrophobic materials exhibit little or no favorable interaction with water and are generally not appreciably soluble in water or similarly polar solvents. The hydrophobic or hydrophilic character of a material can also be understood to approximately correlate with results derived from the octanol/water partition test. The original form of this test, involving measurement of the equilibrium concentration of a dissolved substance in a two-phase system of n-octanol and water, as well as a chromatographic method, are de-

scribed in ASTM E-1147-92. $P = C_{\text{octanol}}/C_{\text{water}}$. The hydrophilic or hydrophobic nature of an amine in question can be evaluated by comparing its P value with the P values of other amines, as those listed above, which are known to be appropriately lipophilic materials. For many hydrophobic chemicals, $\log P$ is greater than 0.8, more commonly 0.9 or greater. That of ethylbenzene, as an example, is about 3.1. A listing of $\log P$ values of many chemicals as well as a theoretical discussion of partition coefficients can be found in Leo et al., Chemical Reviews, 71, 6, pp. 528-616 (1971).

[0013] In contrast, "water-soluble" monomers are those that exhibit sufficient solubility in water to benefit from the present invention. Such materials, untreated, typically exhibit at least 1% by weight solubility in water at room temperature, or at least 5% or at least 10% solubility, and a corresponding lack of solubility in an oil or hydrocarbon medium, e.g., less than 1% or less than 0.1% by weight solubility in, for instance, cyclohexane. Water-soluble monomers will also typically have a relatively low value of $\log P$, as described above. For many hydrophilic chemicals, $\log P$ is about 0.8 or less, commonly 0.7 or less. That of acrylic acid, for instance, a water-soluble monomer, is about 0.4. (Likewise, "water-insoluble" monomers will typically exhibit relatively lesser solubility, e.g., less than 5% by weight solubility in water at room temperature, or less than 2% or 1% or 0.5% or even less than 0.1% or 0.01% and will typically have a relatively higher value of $\log P$.)

[0014] Alternatively, the ethylenically unsaturated, water-soluble sulfonic acid monomer can be a styrenic sulfonic acid, which terms include styrene sulfonic acids and styrene sulfonates as well as substituted styrene sulfonic acids and substituted styrene sulfonates. Such materials, in their salt form, are illustrated by the following formula:



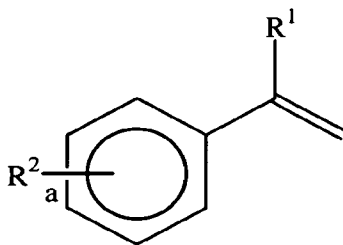
In the above structure, the X^+ is a cation which is an amine ion as described above.

[0015] Other suitable sulfonic acid monomers include sulfoethyl methacrylate, isobutylenesulfonic acid, allylsulfonic acid, vinylsulfonic acid, and amine salts thereof as described above.

[0016] The salt of the water-soluble sulfonic acid and the lipophilic amine can be prepared by any conventional means, such as by the acid-base neutralization reaction of the sulfonic acid and the amine. Alternatively, such salts can be obtained by the combination of a metal salt of the sulfonic acid with another salt (e.g., a halide) of the amine. In the latter case, a metal salt, e.g., a metal halide, will be present as a byproduct, which may be permissible or may be undesirable, depending on the requirements of the polymerization system or downstream product in which the monomers are to be employed. Preparation of the salts of the present invention can be performed in advance of their use in a polymerization reaction, optionally with removal of any byproducts, or the preparation can be in situ, by addition of the reactants to the polymerization mixture.

[0017] The above sulfonic acid monomers are commonly polymerized with one or more lipophilic, water-insoluble monomers. The lipophilic, water-insoluble monomer can be an olefin, and preferably an alpha olefin, of 6 to 18 carbon atoms. Aliphatic alpha olefins of this type include 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, and 1-octadecene, including both linear isomers and branched isomers such as 2-ethylhex-1-ene, and mixtures of linear and branched olefins as may be commercially available.

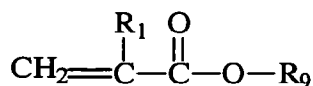
[0018] The lipophilic, water-insoluble monomer can also be styrene (which can also be considered an alpha olefin) or any of the hydrocarbyl-substituted styrenes. Such materials can typically be represented by the formula



In the foregoing structure, R¹ is hydrogen or a hydrocarbyl group, R² is a hydrocarbyl group, and "a" is zero through 5, preferably zero or 1. R¹, if it is a hydrocarbyl group, and R² will each preferably contain 1 to 18 carbon atoms, more preferably 1 to 12, and still more preferably 1 to 4, and the total number of carbon atoms in all such hydrocarbyl substituents will be zero to 3, preferably 0 or 1, and more preferably 0. In addition to the structure shown, with the R¹

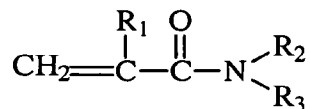
group on the β carbon, it is also possible to have a hydrocarbyl group on the α carbon of the double bond. Such materials are intended to be encompassed by the present invention, although they may be less desirable in some applications due to the reduced polymerization activity of materials containing only internal ethylenic bonds. Similarly, the expression "hydrocarbyl-substituted styrene" is intended to encompass structures in which the R^2 group provides a fused ring structure, that is, in which the overall material is a vinyl naphthalene compound or a hydrocarbyl-substituted derivative thereof. In the latter case, the value of "a" can be up to the number of replaceable hydrogen atoms on the ring structure. Among these alternatives, styrene itself is a preferred monomer.

[0019] The lipophilic, water-insoluble monomer can also be an acrylate ester of the following formula:



where R_1 is a hydrogen or a methyl group and R_9 is a hydrocarbyl group containing 1 to 22 carbon atoms. Examples include methyl acrylate, methyl methacrylate, butyl acrylate, and 2-ethylhexylacrylate.

[0020] The lipophilic, water-insoluble monomer can also be an alkyl substituted acrylamide compound having the formula:



where R_1 is a hydrogen or a methyl group and R_2 and R_3 are independently hydrogen or hydrocarbyl groups, provided that R_2 and R_3 are not both methyl, and the total number of carbon atoms in R_2 and R_3 combined is 2 to 36. Suitable materials include N-phenylacrylamide, N-tert-butylacrylamide, N,N-dibutylacrylamide, N-dodecylacrylamide, and N-octadecylacrylamide.

[0021] Additional comonomers of various types can optionally be present, provided that, at their given concentration they do not interfere with the effectiveness of the present invention. For example, water-soluble monomers generally may be readily polymerizable under certain conditions with 2-acrylamido-2-methylpropanesulfonic acid monomer even in the absence of the present invention, and thus the benefits of the present invention would not be fully expressed. The amounts of such materials should be correspondingly limited.

Alternatively, under other polymerization conditions the water-soluble monomers may not be polymerizable at all and should be avoided entirely. Typical monomers that can be present, in greater or lesser amounts, as the case may be, can include acrylic acid, acrylamide, N-methyl acrylamide, N,N-dimethyl-
5 acrylamide, methacrylic acid, N-vinylpyrrolidone, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate.

[0022] In the polymerization reaction the ethylenic bonds in the styrene or other lipophilic, water-insoluble monomer and in the ethylenically unsaturated, water-soluble polymerizable sulfonic acid monomer polymerize to yield the
10 resulting polymer.

[0023] Examples of solution polymers include poly[styrene-co-2-acrylamido-2-methylpropanesulfonic acid 2-ethylhexylamine salt], polymethylmethacrylate-co-2-acrylamido-2-methylpropanesulfonic acid N,N-dimethyl-n-dodecylamine salt, poly[ethylacrylate/styrene/2-acrylamido-2-methylpropane-
15 sulfonic acid 2-ethylhexylamine salt], poly[butylacrylate/vinyl acetate/2-acrylamido-2-methylpropanesulfonic acid N,N-dimethyl-n-dodecylamine salt], poly-laurylmethacrylate-co-2-acrylamido-2-methylpropanesulfonic acid tri-n-butylamine salt, poly[styrene/maleic anhydride/methyl methacrylate/2-
20 acrylamido-2-methylpropanesulfonic acid 2-ethylhexylamine salt], and poly[1-decene/maleic anhydride/2-acrylamido-2-methylpropanesulfonic acid trioctylamine salt].

[0024] Examples of emulsion polymers include, polymethyl methacrylate/butyl acrylate/2-acrylamido-2-methylpropanesulfonic acid N,N-dimethyl-n-dodecylamine salt, polybutyl acrylate/2-ethylhexyl acrylate/2-acrylamido-2-
25 methylpropanesulfonic acid 2-ethylhexylamine salt, polystyrene-co-2-acrylamido-2-methylpropanesulfonic acid trioctylamine salt, polyvinyl acetate-co-2-acrylamido-2-methylpropanesulfonic acid 2-ethylhexylamine salt, polyethylacrylate/styrene/methacrylic acid/2-acrylamido-2-methylpropanesulfonic
30 acid tri-n-butylamine salt, and polybutyl acrylate/vinyl acetate/2-acrylamido-2-methylpropanesulfonic acid N,N-dimethyl-n-dodecylamine salt.

[0025] The polymerization reaction itself can be a solution polymerization in a hydrophobic medium, or an emulsion polymerization in an aqueous medium. As a variation of solution polymerization, precipitation polymerization has been described in, e.g., U.S. Patent 5,475,047. Any of such polymerizations can be
35 performed in a batchwise, continuous, or semicontinuous manner.

[0026] For solution polymerizations, the hydrophobic medium or solvent can typically be toluene, xylenes, or hexanes. The concentration of the salt of the

lipophilic amine can typically be 0.5% to 50%, or 1 to 20%, or 2 to 10% by weight. Typical catalysts or initiators can include benzoyl peroxide and 2,2'-azobis-(2-methylbutyronitrile), and can be used in amounts of 0.10% to 2%, or 0.05% to 5% by weight. Other materials which can be present include chain transfer agents and foam control agents.. The reaction is typically conducted at 40 to 140°C, preferably 50-110°C, for 1.5 to 8 hours. Conditions for solution polymerizations and variations thereof to suit particular needs and circumstances are within the abilities of those skilled in the art.

[0027] For emulsion polymerizations, the medium is typically water or a predominantly water mixture. The concentration of the salt of the lipophilic amine can typically be 0.1% to 50%, or 0.5 to 40%, or 1 to 20% by weight. Typical catalysts or initiators can include sodium persulfate, potassium persulfate, ammonium persulfate, alkylperoxydicarbonates, and 2,2'-azobis(2-amidinopropane) dihydrochloride, and can be used in amounts of 0.01% to 2.5% or 0.05% to 1% by weight. Other materials which can be present include chain transfer agents, surfactants, foam control agents, buffers, and emulsifiers. The reaction is typically conducted at 40 to 90°C or 50 to 80°C for 1.5 to 8 hours. Conditions for emulsion polymerizations and variations thereof to suit particular needs and circumstances are within the abilities of those skilled in the art.

[0028] Polymers thus prepared can be used in the formation of adhesives, coatings, fillers, or caulks. Such materials typically comprise (a) a resin binder, such as a phenol formaldehyde resin, a urea formaldehyde resin, a melamine formaldehyde resin, or combinations thereof; (b) an emulsion polymer containing the lipophilic amine salt of an ethylenically unsaturated water-soluble polymerizable sulfonic acid, as described above, and (c) optionally an organic solvent and/or water, in conventional amounts that are well known to the person skilled in the art.

EXAMPLES

Example 1 – Amine salt

[0029] Mix 24.8 grams of 2-acrylamido-2-methylpropanesulfonic acid and 151 grams acetone together in a ½ L jar with an electrical stirrer to form a slurry. Add 25.6 grams of N,N-dimethyl-n-dodecylamine via pipette over 30 minutes, adding a portion about every five minutes. No significant temperature increase is noted during the amine addition and the reaction is run at about 18°C (64°F). The slurry starts to clear up at the end of the amine addition and all of the 2-acrylamido-2-methylpropanesulfonic acid is solubilized one hour after the amine addition is completed. Add 0.05 grams of para-methoxyphenol to the jar

contents and the mixture is stirred another hour at room temperature. The jar contents are vacuum filtered through paper using a Buchner funnel. The filtrate is vacuum stripped of acetone and other volatiles using a rotary evaporator at 32°C (90°F) for 40 minutes. One obtains 50.4 grams of a clear viscous liquid.

5 NMR analysis confirms the 2-acrylamido-2-methylpropanesulfonic acid / N,N-dimethyl-n-dodecylamine salt structure.

Example 2 – Amine salt

[0030] Mix 31.0 grams of 2-acrylamido-2-methylpropanesulfonic acid and 151 grams acetone together in a ½ L jar with an electrical stirrer to form a slurry. Add 19.4 grams of 2-ethylhexylamine via pipette over 30 minutes, adding a portion about every five minutes. A slight temperature increase (from 18°C (64°F) to 23°C (74°F)) is noted during the amine addition. The slurry starts to clear up at the end of the amine addition and all of the 2-acrylamido-2-methylpropanesulfonic acid is solubilized one hour after the amine addition is completed. Add 0.05 grams of para-methoxyphenol to the jar contents and the mixture is stirred another hour at room temperature. The jar contents are vacuum filtered through paper using a Buchner funnel. The filtrate is vacuum stripped using a rotary evaporator at 32°C (90°F) for 1.5 hours and 49°C (120°F) for 30 minutes. One obtains 52.4 grams of a clear light yellow viscous liquid.

15 NMR analysis confirms the 2-acrylamido-2-methylpropanesulfonic acid / 2-ethylhexylamine salt structure.

Example 3 – Amine salt

[0031] Mix 24.8 grams of 2-acrylamido-2-methylpropanesulfonic acid and 151 grams acetone together in a ½ L jar with an electrical stirrer to form a slurry. Add 22.2 grams of tri-n-butylamine via pipette over 30 minutes, adding a portion about every five minutes. No significant temperature increase is noted during the amine addition and the reaction is run at about 18°C (64°F). The slurry starts to clear up at the end of the amine addition and all of the 2-acrylamido-2-methylpropanesulfonic acid is solubilized one hour after the amine addition is completed. Add 0.05 grams of para-methoxyphenol to the jar contents and stir the mixture another hour at room temperature. The jar contents are vacuum filtered through paper using a Buchner funnel. The filtrate is vacuum stripped of acetone and other volatiles using a rotary evaporator at 32°C (90°F) for 60 minutes. One obtains 46.8 grams of a semi-viscous pink liquid.

30 NMR analysis confirms the 2-acrylamido-2-methylpropanesulfonic acid / tri-n-butylamine salt structure.

Example 4 -- Polymerization

[0032] A monomer mixture of methyl methacrylate (380 grams) and butyl acrylate (312 grams) is prepared. To a nitrogen-purged solution of sodium lauryl sulfate (0.36 grams) and sodium bicarbonate (1.4 grams) in 403 grams of water at 80°C is added 10% of the monomer mixture and 2 grams of the 2-acrylamido-2-methylpropanesulfonic acid / N,N-dimethyl-n-dodecylamine salt prepared as in Example 1. After the temperature returns to 80°C, a solution of sodium persulfate (0.7 grams) in 10 grams of water is added. After 30 minutes, the remainder of the monomer mixture is added at a steady rate simultaneously adding 20 grams of the 2-acrylamido-2-methylpropanesulfonic acid / N,N-dimethyl-n-dodecylamine salt over the same time period. After 30 minutes of monomer addition, a solution of sodium persulfate (3.5 g, 14.7 mmol) in 140 g of water is added at a steady rate. When addition of all of the ingredients is complete, the resulting latex is stirred under nitrogen for an additional 30 minutes, decanted and cooled.

Example 5 -- Polymerization

[0033] To a two-liter 4-neck reaction flask equipped with a stirrer, nitrogen inlet, thermowell, addition funnel, and a water-cooled condenser is charged 1/3 by volume of a mixture of 288.5 grams of butyl acrylate, 138.2 grams of 2-ethylhexyl acrylate, 20 grams of the 2-acrylamido-2-methylpropanesulfonic acid / N,N-dimethyl-n-dodecylamine salt of Example 1, 3.0 grams of benzoyl peroxide, and 426.7 grams of toluene. The remaining 2/3 of the above mixture is charged to a one-liter addition funnel and purging of the flask with nitrogen is begun. Heat flask contents to 50°C. Within ten minutes, vigorous toluene reflux begins and the temperature increases to 110°C. Add the remaining monomer mixture over 1.5 hours while keeping the temperature at 110°C. Prepare a solution of 1.5 grams benzoyl peroxide in 15 grams toluene and charge this over 5 minutes. Hold the reaction for 2 hours at 110°C while stirring. Cool to room temperature to obtain 890 grams of a clear, viscous polymer solution.

Example 6 -- Polymerization

[0034] To a two-liter, 4-neck reaction flask equipped with a stirrer, nitrogen inlet, thermowell, and water-cooled condenser is charged ethyl acetate (656.1 g), cyclohexane (558.9 g), acrylic acid (276.5 g), stearyl methacrylate (8.5 g) 2-acrylamido-2-methylpropanesulfonic acid / N, N-dimethyl-n-dodecylamine salt of Example 1 (20 g), allyl sucrose (1.7 g) and polyvinyl alcohol (8.5 g). The flask is placed in a constant temperature bath set at 50°C. Stirring is begun and the mixture purged with nitrogen for 30 minutes while the mixture reaches

50°C. Thereafter, initiator (di-(2-ethylhexyl)peroxydicarbonate, 0.5 g) is added. Within 5 minutes the solution becomes hazy as polymer precipitates out of solution. The mixture is maintained for a total of 8 hours at 50°C while stirring, and then is cooled to room temperature. Solvent is removed by rotary evaporation, resulting in a white powder which is the product.

TESTING

[0035] The latex of Example 4 is tested for divalent cation tolerance. Testing is done for calcium coagulation by treating latex with a 5% by weight aqueous CaCl₂ solution. Five grams of the latex from Example 5 requires 40 mL of a 5 wt. % aqueous CaCl₂ solution for coagulation to take place. A latex with no sulfonic acid monomer, but acrylic acid monomer in its place, coagulates with only 1 mL of the 5 wt. % aqueous CaCl₂ solution.

[0036] Testing of the solubility of monomers is conducted by mixing 10% of the monomer with a variety of solvents. Results are shown in the following Table:

Table: Solubility Properties of 2-Acrylamido-2-methylpropanesulfonic acid/Lipophilic Amine Salts (Solubility at 10 % by weight in solvent)

Example	7 (comparative)	8	9	10
Material	2-acrylamido-2-methyl-propane sulfonic acid	Product of Ex. 1	Product of Ex. 2	Product of Ex. 3
Water	clear	clear	clear	clear
Isopropanol	not fully soluble	clear	clear	clear
Ethanol	insoluble	clear	clear	clear
Ethyl Acetate	insoluble	clear	clear	clear
Butyl Acetate	insoluble	clear	trace oil layer on bottom	clear
Toluene	insoluble	clear	oil layer on bottom	oil layer on bottom
Styrene	insoluble	clear	oil layer on bottom	clear

[0037] The results show improved solubility of monomers in solvents of decreasing polarity/increasing hydrophobic character when the salts prepared with hydrophilic amines are tested.

[0038] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0039] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

[0040] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

[0041] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0042] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions can migrate to other acidic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

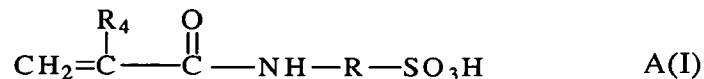
[0043] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reac-

tion conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

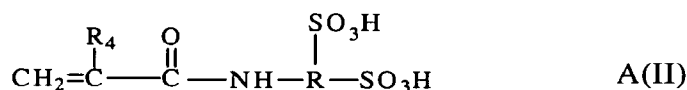
What is claimed is:

1. A method for improving the lipophilic properties of an ethylenically unsaturated water-soluble polymerizable sulfonic acid comprising forming a salt of the ethylenically unsaturated water-soluble polymerizable sulfonic acid with a lipophilic amine.

2. The method of claim 1 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is selected from the group consisting of: acrylamido and methacrylamido sulfonic acids represented by the formulas:

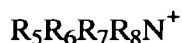


and



wherein R_4 is a hydrogen or a methyl group, R is an aliphatic or aromatic hydrocarbon group.

3. The method of claim 1 wherein the lipophilic amine comprises a material represented by:



where R_5 , R_6 , R_7 , and R_8 are independently hydrogen or hydrocarbyl groups, wherein at least one of R_5 , R_6 , R_7 and R_8 is a hydrocarbyl group.

4. The method of claim 3 wherein the total number of carbon atoms in the amine is about 6 to about 36.

5. The method of claim 1 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is selected from the group consisting of styrenic sulfonic acid and substituted styrene sulfonic acids.

6. The method of Claim 1 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is an unsaturated-hydrocarbylamido-alkanesulfonic acid.

5 7. The method of Claim 1 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is 2-acrylamido-2-methylpropanesulfonic acid.

10 8. The method of Claim 1 where the lipophilic amine is N,N-dimethyl-n-dodecyl amine.

8. The method of Claim 1 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is 2-acrylamido-2-methylpropanesulfonic acid and the lipophilic amine is N,N-dimethyl-n-dodecyl amine.

15 9. A process for improving incorporation of ethylenically unsaturated water-soluble polymerizable sulfonic acid into an emulsion polymer by adding the lipophilic amine salt of said ethylenically unsaturated water-soluble polymerizable sulfonic acid to a latex formulation comprising

20 (a) a lipophilic monomer mixture consisting of one or more water-insoluble lipophilic monomers,

(b) optionally an anionic surfactant,

(c) 0.5 to about 40 weight percent based on the total monomers of a lipophilic amine salt of an ethylenically unsaturated water-soluble polymerizable sulfonic acid,

(d) water,

(e) a polymerization initiator

(f) optionally an ethylenically unsaturated water-soluble polymerizable non-ionic monomer.

30 (g) optionally a chain transfer agent, and

(h) optionally a buffer.

35 10. The process of claim 9 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is 2-acrylamido-2-methylpropanesulfonic acid and the lipophilic amine is N,N-dimethyl-n-dodecyl amine.

11. The process of claim 9 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is 2-acrylamido-2-methylpropanesulfonic acid, the lipophilic amine is N,N-dimethyl-n-dodecyl amine and the ethylenically unsaturated water-soluble polymerizable non-ionic monomer is present and is acrylamide.

12. An adhesive or coating prepared using the process of claim 9.

13. An adhesive, filler or caulk comprising,

(a) a resin binder

(b) an emulsion polymer containing the lipophilic amine salt of an ethylenically unsaturated water-soluble polymerizable sulfonic acid, and

(c) optionally an organic solvent and/or water

14. An adhesive, filler or caulk according to claim 13, wherein said resin binder comprises a phenol formaldehyde resin, a urea formaldehyde resin, a melamine formaldehyde resin, or combinations thereof.

15. A process for improving incorporation of ethylenically unsaturated water-soluble polymerizable sulfonic acid into an organic solvent soluble polymer, comprising adding the lipophilic amine salt of said ethylenically unsaturated water-soluble polymerizable sulfonic acid to a solvent polymer formulation comprising

(a) a lipophilic monomer mixture consisting of one or more water-insoluble lipophilic monomers,

(b) organic solvent,

(c) 0.5 to about 40 weight percent based on the total monomers of a lipophilic amine salt of an ethylenically unsaturated water-soluble polymerizable sulfonic acid,

(d) a polymerization initiator, and

(e) optionally a chain transfer agent.

16. The process of claim 13 where the ethylenically unsaturated water-soluble polymerizable sulfonic acid is 2-acrylamido-2-methylpropanesulfonic acid and the lipophilic amine is N,N-dimethyl-n-dodecyl amine.

ABSTRACT

5 The lipophilic properties of an ethylenically unsaturated water-soluble polymerizable sulfonic acids are improved by forming a salt thereof with a lipophilic amine.